

# Synthesis, Crystal Structure, Theoretical Calculations, and Photoluminescent Property of a Mn(II) Complex Assembled by 5-Amino-isophthalic Acid and Phen Ligands

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**ABSTRACT** A coordination polymer  $[\text{Mn}_2(\text{ctpt})_2(\text{aic})_2]_n$  (**1**,  $\text{ctpt}$  = 2-(4-chloro-phenyl)-1H-1,3,7,8-tetraaza-cyclopenta[1]phenanthrene,  $\text{H}_2\text{aic}$  = 5-amino-isophthalic acid) was hydrothermally designed and synthesized. The complex was characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction, and thermogravimetric analysis (TGA). Each Mn(II) atom is linked by the aic ligands with neighbor Mn(II) atoms, forming an infinite one-dimensional (1D) double-chain structure. Complex **1** crystallizes in monoclinic, space group  $C2/c$ , with  $a = 18.23(1)$ ,  $b = 17.27(1)$ ,  $c = 16.69(1)$  Å,  $V = 4814.0(7)$  Å<sup>3</sup>,  $\text{C}_{27}\text{H}_{16}\text{ClMnN}_5\text{O}_4$ ,  $M_r = 564.84$ ,  $D_c = 1.559$  g/cm<sup>3</sup>,  $\mu(\text{MoK}\alpha) = 0.706$  mm<sup>-1</sup>,  $F(000) = 2296$ ,  $Z = 8$ , the final  $R = 0.0487$  and  $wR = 0.1269$  ( $I > 2\sigma(I)$ ). The 1D chain structure of complex **1** is stable below 458 °C. In addition, to elucidate the essential electronic characters of this complex, theoretical calculation analysis of **1** was performed by the PBE0/LANL2DZ method in Gaussian 03 Program.

**Keywords:** Mn(II) complex; crystal structure; fluorescence; 5-amino-isophthalic acid; theoretical calculation;

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## 1 INTRODUCTION

Coordination polymers with bridged transition metals have received intense interest and attention for their fascinating architectures and potential applications as materials in optical, electronic, magnetic fields, gas

storage, catalysis and so on<sup>[1-5]</sup>. Consequently, numerous new complexes can be specially designed by the careful selection of metal centers with preferred coordination geometries<sup>[6-9]</sup>. It has been observed that organic ligands play crucial roles in the preparation of some interesting coordination networks, such as flexibility, donating type, and the geometry of organic ligands<sup>[10-11]</sup>. Among various organic ligands, aromatic carboxylates have been extensively used because of their extension ability in both covalent bonding and supramolecular interactions (H-bonding and aromatic stacking). For example, 1,3-benzenedicarboxylate, 1,4-benzenedicarboxylate, 1,2-benzenedicarboxylate, 1,3,5-benzenetricarboxylate, and 1,2,3,5-benzene tetracarboxylate are well used in the construction of MOFs due to their structural rigidity, chemical stability and appropriate connectivity. Meanwhile, the polycyclic aromatic bidentate ligands like 2,2'-bipyridine and 1,10-phenanthroline are frequently used corporately with polycarboxylates, leading to many novel architectures.

As a continuation of our previous work, here we synthesize a new ligand 2-(4-chloro-phenyl)-1H-1,3,7,8-tetraaza-cyclopenta[1]phenanthrene (ctpt), based on which together with aic, a novel 1D complex  $[\text{Mn}_2(\text{ctpt})_2(\text{aic})_2]_n$  (**1**) has been synthesized. Further, the thermal stability and luminescent property of **1** have also been investigated.

## 2 EXPERIMENTAL

### 2.1 Generals

With the exception of ligand ctpt, all the other chemicals were commercially available and used as purchased. IR spectrum was carried out on a Perkin-Elmer Spectrum One FTIR spectrometer. Elemental analyses of C, H and N were performed on a PE-2400 elemental analyzer. Thermogravimetric analysis (TG) was performed using a Perkin-Elmer TG-7 analyzer in nitrogen atmosphere. Crystal structure determination was carried out on a Bruker SMART APEX II CCD X-ray diffractometer. The emission spectra were recorded on a FLSP 920 Edinburgh fluorescence spectrometer.

### 2.2 Synthesis of complex 1

Complex **1** was prepared as follows: ctpt (0.099 g, 0.3 mmol),  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (0.051 g, 0.3 mmol), and aic (1.000 g, 0.6 mmol) were dissolved in distilled water (15 mL), and NaOH was added until the pH value of the system was adjusted to about 8.0. The resulting solution was stirred for about 0.5 h at room temperature, sealed

in a 30-mL Teflon-lined stainless-steel autoclave and heated at 170 °C for three days, and finally cooled to room temperature at a rate of 5 °C/ h. The yellow crystals of **1** were collected in 78% yield based on Mn.  $C_{27}H_{16}ClMnN_5O_4$ : calcd. C, 57.36; H, 2.83; N, 12.39%. Found: C, 57.38; H, 2.81; N, 12.51%. IR (KBr,  $cm^{-1}$ ): 3435(s), 1620(s), 1556(vs), 1344(vs), 1205(s), 1074(s), 779(s), 714(s).

### 2.3 X-ray structure determination

A selected yellow crystal with approximate dimensions of 0.45mm × 0.38mm × 0.33mm was mounted on a glass fiber. The diffraction data were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2) K in the range of  $1.70 \leq \theta \leq 25.03^\circ$ . A total of 13736 reflections were collected and 4244 were independent with  $R_{int} = 0.0657$ . The data were corrected for  $Lp$  factors. The crystal structure was solved by direct methods with SHELXS-97<sup>[12]</sup> and refined with SHELXL-97<sup>[13]</sup> by full-matrix least-squares techniques on  $F^2$ . All non-hydrogen atoms were refined anisotropically and all hydrogen atoms isotropically. All the hydrogen atoms attached to carbon were generated geometrically.

## 3 RESULTS AND DISCUSSION

### 3.1 Description of the structure

Single-crystal X-ray diffraction analysis reveals that the title complex crystallizes in the  $C2/c$  space group. Selected bond distances and bond angles are presented in Table 1.

X-ray single-crystal diffraction analysis reveals that complex **1** is a 1D double-chain structure. As shown in Fig. 1, the coordination of Mn atom can be described as a distorted tetragonal pyramid geometry. Each  $Mn^{II}$  atom in **1** is coordinated by three carboxylate oxygen atoms from three distinct aic ligands, and two nitrogen atom donors from one chelating ctpt ligand. The bond distances of Mn–O in **1** are from 2.041(3) to 2.102(3) Å, and those of Mn–N fall in the 2.247(4)~2.278(4) Å range. The O(N)–Mn–N(O) angles are from 88.42(1) to 156.80(1)°. The Mn–O/N bond lengths are all consistent with the corresponding values found in literatures<sup>[14-18]</sup>.

It is interesting that the aic ligand coordinates to three Mn ions through three carboxylic oxygen atoms in a mono-bridging fashion, which gives rise to a 1D double-chain structure (Fig. 2). It should be mentioned that in the unit of **1** two types of rings are formed: the 8-membered ring (the angle of O(3)–Mn(1)–O(4) is 97.727° ;

and the distance of Mn $\cdots$ Mn is 3.849 Å) and the 16-membered ring (the angle of O(1)–Mn (1)–O(3) is 91.756 °, and the distance of Mn $\cdots$ Mn is 7.953 Å).

There are strong N–H $\cdots$ O hydrogen bonding interactions observed in complex **1**, which play an important role in stabilizing the network structure and form a higher dimensional structure. As illustrated in Fig. 3, the existence of N–H $\cdots$ O (H(3A) $\cdots$ O(4) = 1.86 Å, N(3) $\cdots$ O(4) = 2.702 Å and N(3)–H(3A) $\cdots$ O(4) = 165 °) hydrogen bonds leads to the construction of a 3D supramolecular network.

### 3.2 Thermal analysis

To characterize the thermal stability of complex **1**, TG curves have been obtained from crystalline samples in the flowing nitrogen atmosphere at a heating rate of 10 °C/min (Fig. 4). As expected, complex **1** exhibits two steps of weight loss. The first one corresponding to the removal of aic ligand is 30.10% (calcd. 31.75%) from 458 to 479 °C, and the second one due to the departure of ctpt ligand is 58.90% (calcd. 58.50%) in the temperature range of 479~804 °C. The final formation of the metal oxide is maybe MnO. The thermal analysis result suggests the one-dimensional chain structure of anhydrous complex **1** is stable below 458 °C.

### 3.3 Photoluminescent properties

Luminescence property is very important in photochemistry and photophysics. So in this study, we research the luminescence of **1**, as well as the free ligands (Fig. 5). Complex **1** shows one strong emission band at 514 nm (excitation at 320 nm). To further analyze the nature of these emission bands, the emission properties of aic and ctpt ligands are also investigated under the same experimental conditions. The free ligand ctpt exhibits one emission band at 495 nm, and aic exhibits one emission band at 438 nm (excitation at 320 nm). Complex **1** is red-shifted by 19 nm relative to the ctpt ligand, and red-shifted by 76 nm relative to that of aic. The emission bands for the free ligands are probably attributable to the  $\pi^*$ -n transitions. Complex **1** may be a good candidate for potential photoluminescence materials, because it is highly thermally stable and insoluble in water and common organic solvents.

### 3.4 Theoretical calculations

To elucidate the essential electronic characters of this complex, the theoretical calculation was performed by density functional theory (DFT)<sup>[19]</sup> functional with Gaussian 09 program<sup>[20]</sup>, LANL2DZ basis set for Mn atom and 6-31g(d) basis set for all other atoms. The geometric parameters from X-ray diffraction analysis were used as the starting point. There was no symmetry constraint on this complex. The density diagrams of the

highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of Mn complex in ground state are calculated and shown in Fig. 6.

For complex **1**, HOMO and LUMO both reside on the aniline ligands. HOMO distributes as low as 0.5% over the  $d$  orbital of each Mn atom, whereas the  $d$  orbitals of Mn atoms make hardly any contribution for LUMO. The attached phenanthroline derivative ligands of electron rich properties are helpful to electron-transporting. Therefore, HOMO is distributed mainly over one phenanthroline derivative ligand, while LUMO is localized mainly on another phenanthroline derivative ligand. Each phenanthroline derivative ligand contributes to HOMO or LUMO as high as 98%.

## 4 CONCLUSION

In conclusion, a new complex has been hydrothermally synthesized, and structurally characterized by elemental analysis, IR spectrum, TG, and single-crystal X-ray diffraction. Complex **1** has high thermal stability and is worthy of further study as candidate of potential photoluminescence material.

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**Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for 1**

Bond	Dist.	Bond	Dist.
Mn(1)–O(1)	2.102(3)	Mn(1)–O(3)	2.041(3)
Mn(1)–O(2) <sup>ii</sup>	2.050(3)	Mn(1)–N(1)	2.278(4)
Mn(1)–N(2)	2.247(4)		
Angle	(°)	Angle	(°)
O(3)–Mn(1)–O(2) <sup>ii</sup>	111.70(1)	O(3)–Mn(1)–O(1)	91.77(1)
O(2) <sup>ii</sup> –Mn(1)–O(1)	97.74(1)	O(3)–Mn(1)–N(2)	107.94(1)
O(2) <sup>ii</sup> –Mn(1)–N(2)	139.53(1)	O(1)–Mn(1)–N(2)	88.81(1)
O(3)–Mn(1)–N(1)	106.76(1)	O(2) <sup>ii</sup> –Mn(1)–N(1)	88.42(1)
O(1)–Mn(1)–N(1)	156.80(1)	N(1)–Mn(1)–N(2)	72.49(1)

Symmetry code: ii:  $-x, y, -z+3/2$

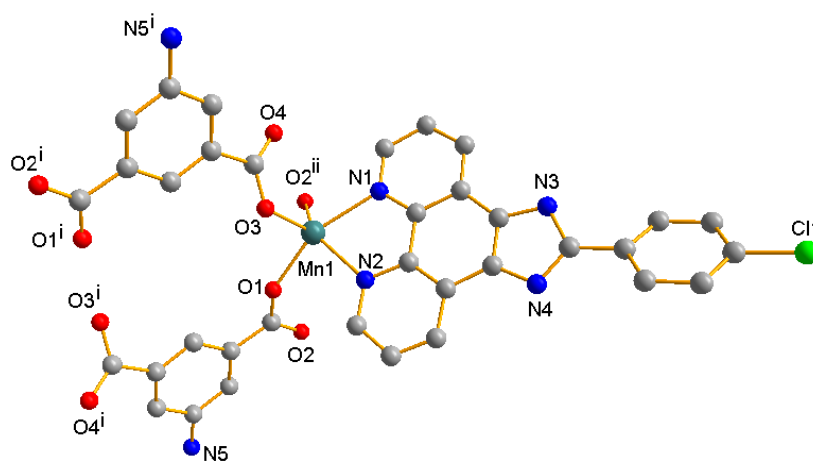


Fig. 1. Coordination environment of the Mn ions with H atoms  
and ctpt omitted for clarity (i:  $-x, -y, 1-z$ ; ii:  $-x, y, -z+3/2$ )

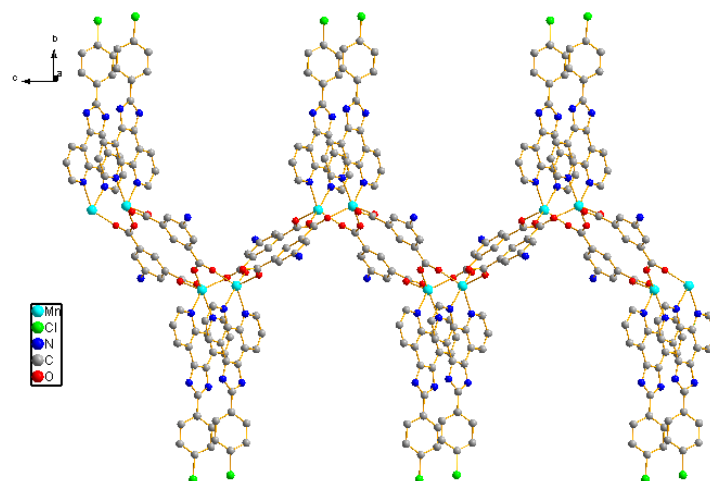


Fig. 2. One-dimensional chain structure of complex 1 (Hydrogen atoms were omitted)

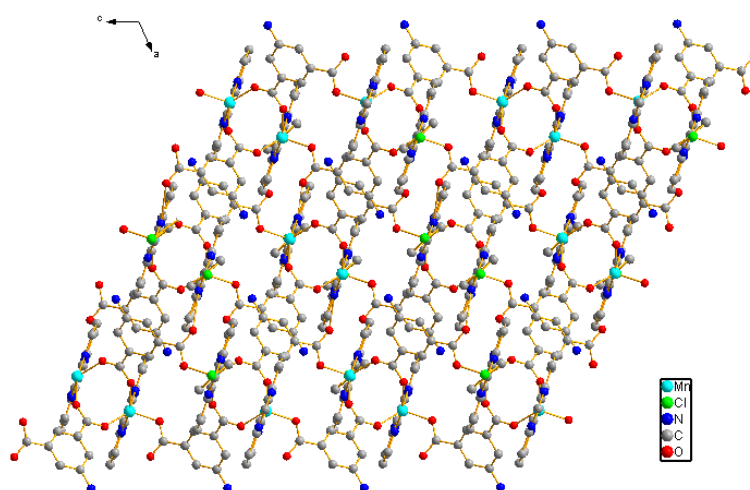


Fig. 3. 3D framework structure of complex 1 in the  $ac$  plane (Hydrogen atoms were omitted)

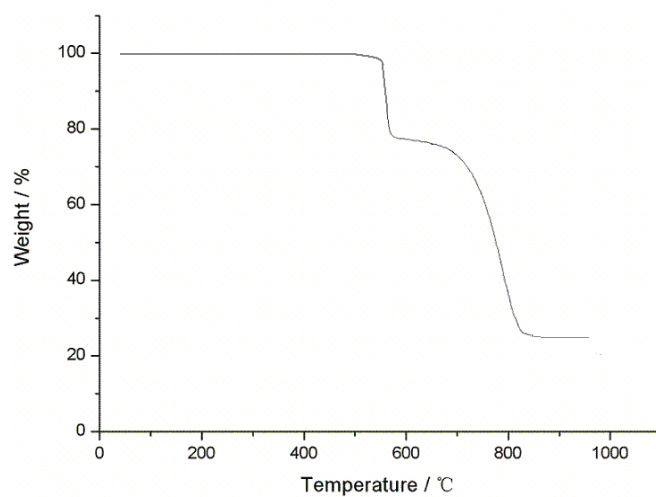


Fig. 4. TG plot of complex 1

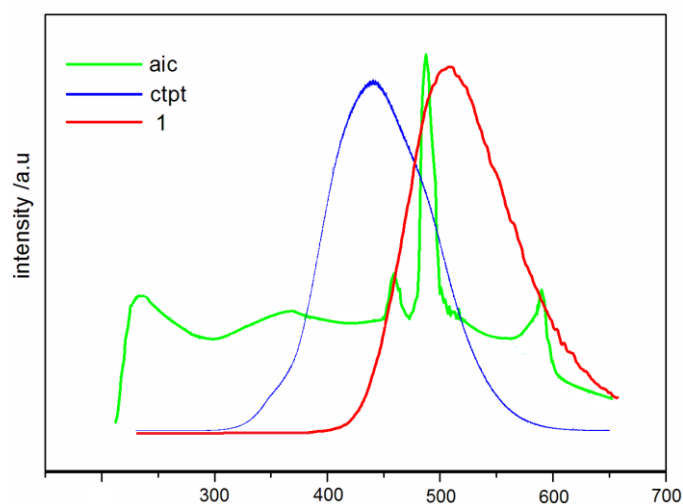


Fig. 5. Luminescent spectrum of the ligand and complex 1 in solid state at room temperature

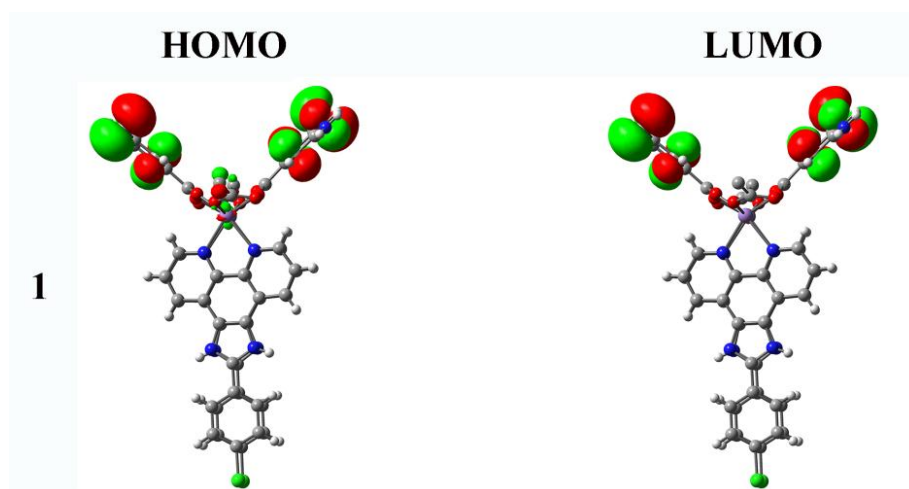


Fig. 6. Frontier molecular orbital of complex 1



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